

PATENT ABSTRACTS OF JAPAN

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**(54) POSITIVE TYPE PHOTORESIST COATING SOLUTION FOR PRODUCTION OF
LIQUID CRYSTAL ELEMENT AND SUBSTRATE USING THE SAME**

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a positive type photoresist coating solution for a liquid crystal element which controls striation, unevenness in drying and traces of dropping in a well-balanced state.

SOLUTION: (a) An alkali-soluble resin, (b) a quinonediazido group-containing compound and (c) a nonionic fluorine-and silicon-base surfactant having 10-25 wt.% fluorine content and 3-10 wt.% silicon content are dissolved in (d) an organic solvent to obtain the objective positive type photoresist coating solution for the production of a liquid crystal element. A substrate is coated with the coating solution.

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CLAIMS

[Claim(s)]

[Claim 1] (a) Positive type photoresist coating liquid for liquid crystal device manufacture which comes to dissolve the nonionic fluorine and silicon system surface active agent alkali fusibility resin and whose (b) quinone diazide radical content compound **** (c) fluorine content are 10 - 25 % of the weight and, whose silicon content is 3 - 10 % of the weight in the (d) organic solvent.

[Claim 2] (c) Positive type photoresist coating liquid for liquid crystal device manufacture according to claim 1 whose components are the nonionic fluorine and silicon system surface active agent which the fluorination alkyl group, the alkyl siloxane radical, and the alkyleneoxy radical combined.

[Claim 3] (c) Positive type photoresist coating liquid for liquid crystal device manufacture according to claim 1 or 2 which comes to blend a component 0.2 to 1% of the weight to solutes other than the (c) component of this coating liquid.

[Claim 4] (d) Positive type photoresist coating liquid for liquid crystal device manufacture given in claim 1 thru/or any 1 term of 3 chosen from the group which an

organic solvent becomes from a propylene-glycol-monomethyl-ether acetate independent solvent, the partially aromatic solvent of ethyl lactate and butyl acetate, and the partially aromatic solvent of ethyl lactate and propylene-glycol-monomethyl-ether acetate.

[Claim 5] The base material which applied and dried the positive type photoresist coating liquid for liquid crystal device manufacture given in claim 1 thru/or any 1 term of 4 on the glass angle substrate, and prepared the resist film.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the base material which used the positive type photoresist coating liquid for liquid crystal device manufacture, and it. In more detail, this invention relates to the positive type photoresist coating liquid which controls striae SHON, the drying mark, and the remains of dropping with sufficient balance, and the base material using it, also when it applies to the liquid crystal device base material of a large-scale method.

[0002]

[Description of the Prior Art] Adding various surfactants to a positive type photoresist for striae SHON (striped pattern of radial) prevention, as it is in JP,7-230165,A conventionally is performed idiomatically. However, if it is large-sized and the glass angle substrate for liquid crystal device manufacture is replaced, a problem like 360mmx460mm, 550mmx650mm, and 600mmx720mm that a lepidic form pattern (drying mark of the resist film) appears everywhere in addition to the problem of striae SHON has arisen from the silicon wafer for semiconductor device manufacture in a substrate. This drying mark produces a hundreds of A resist thickness difference, and such a thickness difference has been the technical problem which cannot be disregarded in the liquid crystal device as which detailed-ization is demanded recently in order to put the dimension of the resist pattern obtained out of order. Such striae SHON and the drying mark can be prevented to some extent by adding the fluorochemical surfactant which has a fluorination alkyl group to a positive resist.

[0003] However, a problem new also about the positive-resist coating liquid which added the fluorochemical surfactant has arisen. That is, centering on a glass angle

substrate, it is formed from a nozzle as the remains of dropping being circular in the dropping section, in case the resist film is subsequently formed by spin spreading, dropping and, and the problem that this does not disappear and remains produces this positive-resist coating liquid. It is surmised that these remains of dropping originate in the fluorine component in an activator remaining into a dropping part, and that improvement is desired, in order to produce a resist thickness difference and to put the dimension of the resist pattern obtained out of order, if these remains of dropping are generated.

[0004]

[Problem(s) to be Solved by the Invention] Therefore, in this invention, excelling in the resist pattern configuration which is the purpose of positive type photoresist constituent original aims from the first to let striae SHON and the drying mark offer the positive type photoresist coating liquid for liquid crystal device manufacture with which generating **** and the remains of dropping do not remain, and the base material using this.

[0005]

[Means for Solving the Problem] That is, in this invention, the purpose of this invention was attained by adding the nonionic fluorine and silicon system surfactant which has a specific fluorine and a specific silicon content. The purpose of this invention was attained by offering the positive type photoresist coating liquid for liquid crystal device manufacture which specifically comes to dissolve the nonionic fluorine and silicon system surface active agent (a) alkali fusibility resin and whose (b) quinone diazide radical content compound **** (c) fluorine content are 10 – 25 % of the weight and, whose silicon content is 3 – 10 % of the weight in the (d) organic solvent.

[0006]

[Embodiment of the Invention] Each component which constitutes the positive type photoresist coating liquid for liquid crystal device manufacture of this invention is explained below.

(a) If used for the conventional positive type photoresist constituent about the component (alkali fusibility resin), it will not be limited especially. Especially a desirable thing is cresol novolak resin of weight average molecular weight 3000–15000 which at least one sort of phenols chosen from p-cresol, m-cresol, a xylenol, and a trimethyl phenol are made to react with the aldehydes like the bottom of an acid catalyst, and formaldehyde, and is obtained, when sensibility, definition, and a resist pattern configuration are taken into consideration.

[0007] (b) About a component (quinone diazide radical content compound), a quinone

diazide radical content compound will not be especially limited, if it is the compound which has the quinone diazide radical known as a photosensitive component of a positive type photoresist until now. Such a compound For example, a naphthoquinone -1 and 2-diazido-(4 or 5) sulfonyl halide, Polyhydroxy benzophenones, such as a 2, 3, 4-trihydroxy benzophenone, 2, 3 and 4, and 4'-tetra-hydroxy benzophenone; A bis(4-hydroxy - 3, 5-dimethylphenyl)-2-hydroxy phenylmethane, A bis(4-hydroxy - 2, 5-dimethylphenyl)-2-hydroxy phenylmethane, A bis(4-hydroxy - 2, 3, 5-trimethyl phenyl)-2-hydroxy phenylmethane, A bis(4-hydroxy - 2, 3, 5-trimethyl phenyl)-3-hydroxy phenylmethane, A bis(4-hydroxy - 2, 3, 5-trimethyl phenyl)-4-hydroxy phenylmethane, A screw (4-hydroxy-2-methyl-5-cyclohexyl phenyl) -3, a 4-hydroxy phenylmethane, A bis(4-hydroxy-2-methyl-5-cyclohexyl phenyl)-4-hydroxy phenylmethane, It can manufacture by carrying out the condensation reaction of tris phenols; such as 1-[1-(4-hydroxyphenyl) isopropyl]-4-[1 and 1-bis(4-hydroxyphenyl) ethyl] benzene, and perfect-esterifying or partial esterifying. Especially a desirable thing is a naphthoquinone -1, excellent [which 3.5 mols of 2-diazido-5-sulfonic-acid chloride were made to react, and obtained it from 2.0] in the property of a definition **** pattern configuration to one mol of 2, 3, 4, and 4'-tetra-hydroxy benzophenones, and desirable.

[0008] (C) the ion chromatography after making fluorine ion form with the fluorine content [need / the (c) component of this invention / about a component (nonionic surfactant) / for a fluorine content to be 10 - 25 % of the weight, and to be the nonionic fluorine and silicon system surfactant whose silicon content is 3 - 10 % of the weight] in this activator -- moreover, a silicon content is a numeric value calculated by the inductively-coupled-plasma-atomic-emission-spectrometry method (ICP). A fluorine content heats a sample with an electric furnace, and after it burns carbon and hydrogen and generates fluorine ion, it more specifically carries out a quantum with ion chromatography. Moreover, a silicon content prepares a sample as a solid-state or a solution, and it carries out a quantum by the ICP method.

[0009] Although adding various surfactants to a positive resist is known as the term of a Prior art also described What is used preferably especially Trade name Fluorad FC-430, FC-431 A perfluoroalkyl radical [(like / Sumitomo 3M)] And an alkyleneoxy radical Nonionic fluorochemical surfactant; which it has Trade name SI-10 series Megger fuck pane TADDO 31 (The Takemoto fats-and-oils company make) The nonionic silicon system surfactant which the alkyl siloxane radical [(like / by) Dainippon Ink & Chemicals, Inc.] and the alkyleneoxy radical combined; The trade name megger fuck R-08, There are a nonionic fluorine, a silicone system surfactant,

etc. which a perfluoroalkyl ester group like trade name XRB-4 (Dainippon Ink & Chemicals, Inc. make), the alkyl siloxane radical, and the alkyleneoxy radical combined. In addition, the fluorine content of the above-mentioned megger fuck R-08 is 9.0 % of the weight, a silicon content is 3.0 % of the weight, and they are 5.0 % of the weight and 1.7 % of the weight about XRB-4, respectively.

[0010] However, for example, when a nonionic fluorochemical surfactant is used, the remains of dropping are formed. Moreover, in the case of a nonionic silicon system surface active agent, in addition to the remains of dropping, the part (called an edge bead) into which resist thickness rises is formed near a substrate edge. Moreover, if the case of R-08 or XRB-4 is compared with the above-mentioned fluorochemical surfactant or a silicon system surfactant, the remains of dropping, striae SHON, and the drying mark are unsatisfying although improved. Moreover, if the substrate size to be used is enlarged, it will not come to improve.

[0011] Desirable fluorine contents and silicon contents are 15 - 25 % of the weight, and 5 - 10 % of the weight, respectively, and that [its] it is 2 to 5 times whose fluorine content to a silicon content of this is desirable rather than it controls striae SHON, the drying mark, and the remains of dropping of this application (C) component with sufficient balance. Although it is not especially limited if the (C) component of this invention is in the above-mentioned range, the following nonionic fluorine and silicon system surfactant are mentioned as an example of a suitable thing. There are a nonionic fluorine, a silicone system surfactant, etc. which a trade name X-70-090, X-70-091, X-70-092, a perfluoroalkyl radical like X-70-093 (all are the Shin-Etsu Chemical Co., Ltd. make), the alkyl siloxane radical, and the alkyleneoxy radical combined. These fluorine contents are 21 % of the weight, and a silicon content is 7 % of the weight.

[0012] The substrate used for this invention will be increasingly enlarged from now on, although it is a glass angle substrate for liquid crystal device manufacture and 600mmx720mm etc. is specifically used for 360mmx460mm to 550mmx650mm, and a pan. As for such a large-sized glass angle substrate, although the magnitude of a substrate also differs, since the conditions on the front face of a substrate -- various kinds of film, such as the chromium film, the molybdenum film, the molybdenum alloy film, the tantalum film, tantalum alloy film, a silicon nitride film, amorphous silicon film, indium oxide (ITO) film that doped tin oxide, and a tin oxide film, is formed -- differ to the substrate, the POJIRE cyst POJIREJISUTO for semiconductor device manufacture and for liquid crystal device manufacture differs from the silicon wafer of semiconductor device manufacture technically.

[0013] (c) As for the loadings of a component, it is desirable to add preferably 0.2 to 1% of the weight to (solutes other than the (c) component of this coating liquid, for example, (a), and b) and the other additives mentioned later in 0.2 to 0.5% of the weight of the range. In order to raise the wettability to a developer about this amount especially in semiconductor device manufacture, it needed to use in about 0.025% of the weight of small quantity, but like this invention, in order to control the drying mark especially in the large-sized glass angle substrate for liquid crystal device manufacture etc., using in the above-mentioned range is desirable.

[0014] (d) If it is proposed as an organic solvent of a positive type photoresist about the component (organic solvent) until now, it will not be limited especially. Specifically, mono-OKIJI carboxylic-acid alkyls, such as ketones; methyl lactates, such as acetic-acid alkyl; acetones, such as polyhydric-alcohol derivative; methyl acetate, such as monomethyl of ethylene glycol, propylene glycol, and ethylene glycol mono-acetate and propylene glycol mono-acetate, monoethyl, monopropyl, and the monobutyl ether, ethyl acetate, and butyl acetate, a methyl ethyl ketone, a cyclohexanone, and 2-heptanone, ethyl lactate, methyl METOKI dipropionate, and ethyl ETOKI dipropionate, or the derivative of those is mentioned.

[0015] These may mix and use two or more sorts if needed. Especially a desirable thing is the partially aromatic solvent of a propylene-glycol-monomethyl-ether acetate independent solvent, ethyl lactate, the partially aromatic solvent of butyl acetate and ethyl lactate, and propylene-glycol-monomethyl-ether acetate especially. 70 - 90 % of the weight of ethyl lactates, 30 - 10 % of the weight of butyl acetate, and the latter mixed rate of the former mixed rate are 60 - 90 % of the weight of ethyl lactates, and 10 - 40 % of the weight of propylene-glycol-monomethyl-ether acetate. Moreover, when the above-mentioned solvent is made to mix 2 - 40 % of the weight of gamma-butyrolactone if needed, the preservation stability of a positive-resist solution improves and it is much more desirable.

[0016] Addition components, such as a hydroxyalkyl nitrogen-containing heterocyclic compound like 2-hydroxyethyl pyridine as a with a weight average molecular weight of about 200 to 600 low-molecular-weight phenol or an adhesion improver like the tris phenols which are the esterified objects used for the above-mentioned (b) component for raising other additives, others, and sensibility, and an antihalation agent which has exposure absorption-of-light ability further, may be blended if needed.

[0017]

[Example] Hereafter, although an example explains this invention further, it is not limited to these. In addition, the following approaches estimated many physical

properties of the obtained positive type photoresist coating liquid.

(1) Spinner spreading of the positive type photoresist coating liquid which, : was prepared was carried out so that it might become 1.5 micrometers of thickness on the 360mmx460mm glass angle substrate with which Cr film was formed, and the resist paint film was formed. [striae] Subsequently, temperature of a hot plate was made into 130 degrees C, spacing of about 1mm was opened, 1st desiccation was performed for 60 seconds, subsequently 110 degrees C of 2nd desiccation were performed for 60 seconds on the hot plate, and the resist film was obtained. The substrate with which this resist film was formed was observed by viewing, what striae SHON has not generated was made into O, and generating of striae SHON made the intense thing x, and made few things **.

[0018] (2) The resist film was observed by viewing like drying-mark: (1), O and generating made the intense thing x for what the drying mark has not generated, and few things were made into **.

[0019] (3) [0020] which observed the resist film by viewing like remains of dropping: (1), made O that in which the remains of dropping do not remain, and made the extant thing x m-cresol and p-cresol are mixed at a rate of 60:40 by the weight ratio.

(Example 1) The cresol novolak resin (weight average molecular weight 10000) 100 weight section which added formalin to this, condensed with the conventional method using the oxalic acid catalyst, and was obtained, X-70-093 which is the one mol of 2, 3, 4, and 4'-tetra-hydroxy benzophenones, a naphthoquinone -1, and 2.2 mols [of 2-diazo-5-sulfonyl chloride] esterification resultant 27 weight section, and a fluorine and a silicon content activator The 0.38 weight section (0.3 % of the weight) The propylene-glycol-monomethyl-ether acetate 324 weight section, after dissolving in the partially aromatic solvent of the gamma-butyrolactone 36 weight section (weight ratio 9:1), come out of this thing unenthusiastically using the membrane filter of 0.2 micrometers of apertures, and positive type photoresist coating liquid was prepared. The evaluation trial of above-mentioned (1) - (3) was performed about this thing. A result is shown in Table 1.

[0021] (Examples 2-5, examples 1-5 of a comparison) In the example 1, positive type photoresist coating liquid was prepared like the example 1 except having replaced the class, amount, or solvent of an activator with what is shown in Table 1. The evaluation result of above-mentioned [about this thing] (1) - (3) is shown in Table 1.

[0022]

[Table 1]

表 1

実施例 又は 比較例	活性剤 (重量%)	溶剤 (重量比)	ストリーション	乾燥むら	滴下跡
実施例 1	X-70-093 (0.3)	PGMEA : γ -B (9:1)	○	○	○
実施例 2	X-70-093 (0.3)	PGMEA	○	○	○
実施例 3	X-70-093 (0.3)	PGMEA:EL (3/7)	○	○	○
実施例 4	X-70-093 (0.1)	PGMEA	○	△	○
実施例 5	X-70-093 (0.2)	PGMEA	○	○	○
比較例 1	FC-430 (0.05)	PGMEA	○	×	×
比較例 2	S1-10 (0.05)	PGMEA	○	×	×
比較例 3	ペイント*31 (0.05)	PGMEA	○	×	×
比較例 4	R-08 (0.05)	PGMEA	○	×	×
比較例 5	XRB-4 (0.05)	PGMEA	○	×	×

PGMEA : プロピレングリコールモノメチルエーテルアセテート

EL : 乳酸エチル

γ -B : γ -ブチロラクトン

[0023]

[Effect of the Invention] Since this invention was constituted as mentioned above, even if it is in the case where it applies to a large-sized substrate like the glass angle substrate for liquid crystal device manufacture, the positive type photoresist coating liquid which controls striae SHON, the drying mark, and the remains of dropping with sufficient balance can be offered.

[Translation done.]